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Optimizing catalytic tar-deoxygenation of fast pyrolysis vapors

Andreas Eschenbacher, Peter Arendt Jensen, Ulrik Birk Henriksen, Jesper Ahrenfeldt,

Anker Degn Jensen*

DTU Chemical Engineering, Technical University of Denmark (DTU), Kgs. Lyngby, DK-2800, Denmark

*aj@kt.dtu.dk

1 Introduction / Scope

The concept of de-centralized smaller scale pyrolysis plants that locally valorize available biomass by densifying its energy content into a bio-crude is of increasing interest world-wide. Fast pyrolysis of biomass produces a high yield of bio-oil through well-established technologies at optimized temperature, pressure, and residence time of the liberated pyrolysis vapors^{1,2}. Operating conditions and chemical transformations that reduce the oil's oxygen content and acid number to stabilize the oil deserve prioritized attention³ and allow further processing in oil refineries. Deoxygenation can be obtained by catalytic upgrading over solid acid catalysts. A close coupled process operating at similar temperature and atmospheric pressure conditions to those preferred for optimum yields of bio-oil potentially offers economic advantages for zeolite deoxygenation over high pressure hydrotreating⁴.

To date, the medium pore size ZSM-5 zeolite yields a high aromatic yield and the least amount of coke⁵ in upgrading of pyrolysis vapors. However, coke formation in the reaction of pyrolysis vapors over the zeolites and steam dealumination still leads to rapid deactivation⁶⁻⁹. Enhancement of ZSM-5 performance besides optimal Si/Al ratio and operating temperature is obtained by either synthesis modifications, or post-synthesis treatment. Incorporation of Ga to a ZSM-5 catalyst was shown to increase the aromatic yields considerably¹⁰, and the combination of several types of catalysts in order to exploit their unique advantages was demonstrated for physically mixing with mesoporous catalysts¹¹ and dual beds comprised of solid acid and basic catalysts¹³. Despite promising laboratory results, long term experiments of pilot plants showing stable catalyst operation with multiple regeneration steps are needed to prove the economic attractiveness of bio-oil plants.

2 Experimental approach and results

Process optimization of a bench scale ablative type fast pyrolysis set-up (Fig. 1) has been performed in order to screen the performance and stability of modified MFI zeolites in the ex-situ upgrading of straw and wood derived pyrolysis vapors. It is investigated how the operation and interaction of the pyrolysis unit, hot gas filter and catalyst fixed bed influence the product distribution. While mostly nitrogen is used as sweeping gas, the recycling of non-condensable pyrolysis gases may have a positive effect on the oil yield¹⁴ and is currently being investigated.

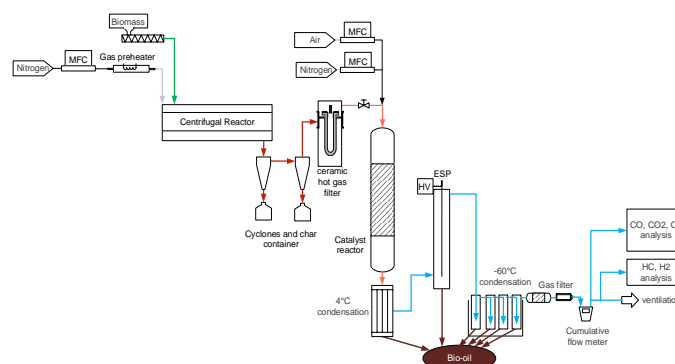


Figure 1: Process scheme of fast pyrolysis set-up with ex-situ vapor upgrading, downstream oil collection and gas analysis

By modifications of the zeolite, this study aims to improve both the active time on stream and the long-term stability throughout multiple regeneration cycles. Both acidity and ratio of micro to mesopores (Fig. 2) are steered towards limited coke formation at maximum valuable product yield. The modified catalysts are analyzed by nitrogen and argon physisorption, NH_3 -TPD, XRD, XRF and TEM analysis in order to better correlate the catalyst activity with its structure and acidity.

The oils are analyzed for water and elemental composition and subjected to GC-MS and SEC analysis. Mass and energy balances are conducted to corroborate the results. Repeated intermittent regeneration of the catalyst was demonstrated, which showed the importance to limit the regeneration temperature in order to prevent loss of catalyst activity. As a next step, hierarchical zeolites will be tested to obtain further insights on how the interplay between pore structure and distribution of acid sites affects catalyst activity. In addition, modifications of the zeolite for enhanced hydrothermal stability are considered in order to speed up the regeneration step.

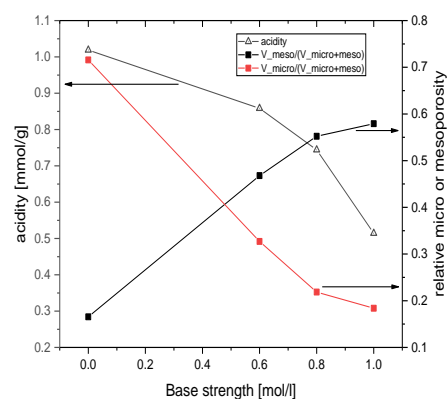


Figure 2: Change in acidity and relative micro/mesopore volume of modified MFI zeolite

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